Journal of Civil Engineering and Architecture 9 (2015) 677-683
doi: 10.17265/1934-7359/2015.06.005

Assessment of the Presence of Chlorides in Mortar through the Silver Nitrate Colorimetric Spraying Method

Victor Correia de Oliveira Pereira[1] and Eliana Cristina Barreto Monteiro[1, 2]

1. Department of Civil Engineering, University of Pernambuco, Recife 50720-001, Brazil

2. Department of Civil Engineering, Catholic University of Pernambuco, Recife 50720-001, Brazil

Abstract: This study aims to evaluate the presence of free chlorides by the silver nitrate colorimetric spraying method in mortars made with Portland cement CP II Z-32. In order to make an assessment beyond the qualitative analysis, a calculation of the contaminated areas by free chlorides was performed by measuring the regions using a computer image analysis software (IMAGEJ). The experimental part of the research involved samples of 5 cm × 10 cm of mortar and 0.1 M solution of silver nitrate in distilled water. The mortar samples were made with cement CP II Z-32 with the following concentrations of chloride incorporated into the mixing water: 0%, 0.4%, 0.6%, 0.8%, 1.0% and 2.0%, in relation to the mass of cement, totaling 108 samples. The average of percentage results from the contaminated area of the series of samples was respectively 0%, 14.9694%, 19.7444%, 46.0239%, 62.3311% and 96.0083% in relation to the total area, concluding that the method of silver nitrate spraying is applicable and that the white color indicates the presence of chloride ions and other possible aggressive salts to the structure or the concrete.

Key words: Silver nitrate, chloride ions, corrosion, colorimetric method.

1. Introduction

The territorial formation of Brazil is based on the system of the occupation of its coast, as in the historical context and the first Portuguese settlements in Brazilian lands were located in the coastal zone, generating high density areas around it, thus constituting the first city networks. Urbanization, industrialization and tourism activities are some of the prior factors for the dynamics of coastal habitat occupation [1].

According to Ref. [2], more than half of the population live at a distance of approximately 60 km from the sea, while 20% of the population of the coastal zone, corresponding to a quota of 42 million inhabitants, in an area of approximately 388,000 km^2.

From the early 20th century on, there was an intensification of the use of concrete in Brazil and for many years, it was believed that this type of material had an unlimited durability, where structures built with this material hardly needed repairs. Between the 1980s and 1990s, pathological manifestations were in evidence due to the speed and frequency in which they appeared, making the concept of unlimited durability of concrete to be reconsidered. Among the main pathologies, the corrosion of the rebars stood out as one of the most important and costly events [3].

The reinforced concrete structures located in the coastal zone are more subject to attacks by chloride ions, originated from the salty spray exposure, the breaking of the sea waves and its splashes. These environmental conditions of severe aggressiveness and very severe aggressiveness imply a higher incidence of rebar corrosion [4].

Pontes et al. [5] verified that structures located at up to 400 m from the sea presented a high content of chloride ions. In a survey [5] conducted in the city of Recife—PE (Pernambuco), the authors presented the relationship between the average deposition of chlorides and the distance from reinforced concrete structures in relation to the sea. The structures that

Corresponding author: Victor Correia de Oliveira Pereira, M.Sc., professor, research fields: concrete, corrosion and materials. E-mail: victor.napster@gmail.com.

were at a distance of 7 m from the sea showed a content of chloride ions of 586.27 mg/m^2 per day, at 100 m, a level of 297.10 mg/m^2 per day was found, at 160 m, the content was of 119.32 mg/m^2 per day, at 230 m the content found was of 35.85 mg/m^2 per day and at 320 m, the level was of 35.87 mg/m^2 per day, showing that the chloride ions were the major causes of the structure depassivation.

The colorimetric method of silver nitrate solution spraying is a practical, easy and very quick assay, while laboratory tests for the identification and quantification of chlorides are costly and time consuming. The silver nitrate spraying test is qualitative and is carried out onsite, which allows to measure the depth of penetration of the free chloride in the concrete structure. The method of the test application is similar to that of the phenolphthalein to determine the depth of carbonatation, using a chemical indicator [6].

The silver nitrate solution spraying test contributes to the technical scope for its practical application and the capacity to identify on the structure of the reinforced concrete the existence of chlorides, thus making it possible to anticipate the choice of the repair technique to be applied, while the results of more discerning tests for the analysis of chlorides are not yet available [7].

2. Materials and Method

2.1 Materials

2.1.1 Portland Cement

Cement CPII-F-32 was used. Tables 1 and 2 present characteristics of the cement (source: the producer).

2.1.2 Silver Nitrate

The silver nitrate used was mixed in a solution with distilled water (0.1 M) to make the reacting compound.

2.1.3 Aggregate

Natural quartzy sand widely found in the region was used. This material was characterized by the specific

Table 1 Chemical characteristics of the cement used.

Chemical composition	Assay	
	Results (%)	Limits of Ref. [8]
Loss on ignition—PF	6.15	< 6.5%
Silicon dioxide—SiO_2	24.01	S.E. (standard error)
Aluminum oxide—Al_2O_3	4.41	S.E.
Iron oxide—Fe_2O_3	2.21	S.E.
Total calcium oxide—CaO	54.14	S.E.
Magnesium oxide—MgO	4.39	≤ 6.5%
Sulphur trioxide—SO_3	2.4	≤ 4.0%
Sodium oxide—Na_2O	0.1	S.E.
Potassium oxide—K_2O	1.45	S.E.
Carbonic anhydride	4.76	< 5.0%
Insoluble residue—RI	12.43	< 16.0%
Free calcium oxide—free CaO	0.81	S.E.

Table 2 Physical and mechanical assays of CPII Z-32.

Physical and mechanical assays			
Assays		Results	Limits of Reference [8]
Fineness	Residues on sieve of 75 μm (%)	3.2	≤ 12.0%
	Residues on sieve of 44 μm (%)	14.1	S.E.
Specific mass (g/cm^3)		2.96	S.E.
Specific area—Blaine (m^2/kg)		506	> 260 (m^2/kg)
Water from the paste of normal consistency (%)		27.6	S.E.
Time	Time of beginning of solidification	03 h 40 min	> 1 h
	Time of end of solidification	04 h 30 min	≤ 10 h (facultative)
Le Chatelier's hot expansibility (mm)		0.5	< 5 mm
Resistance to compression	At the age of 1 day (MPa)	13.1	S.E.
	At the age of 3 days (MPa)	22.0	> 10 MPa
	At the age of 7 days (MPa)	26.5	≥ 20 MPa
	At the age of 28 days (MPa)	35.3	> 32 MPa

Source: data supplied by producer.

and apparent density of the mass, determination of the granulometric curve and the uniformity coefficient in accordance with the method of Allen-Hazem.

2.1.4 Mixing Water

The water used was derived from the supply network of the Pernambuco Sanitation Company.

The result of the chemical analysis of the mixing water to determine the chloride content found was 87.5 mg/L, remaining within the maximum limit standard which is 1,000 mg/L [9].

There was no analysis of the water for the determination of sulphates.

2.2 Method

2.2.1 Quantity of Test Samples

The work was composed of six series of mortar samples, totaling 108 cylindrical samples of mortar with 5 cm base by 10 cm of height, as specified by Ref. [10], being added percentages of kitchen salt (in relation to the weight of cement) to the mixing water.

For each series, 18 cylindrical were confectioned where the presence of free chlorides was evaluated from six samples at three different ages (7, 28 and 56 days after molding). Table 3 details the distribution sample quantities since 0% (reference sample) up to 2%.

The choice for the use of samples with these characteristics is justified by the following factors: easy molding and handling after curing. The test by the silver nitrate spraying method is a qualitative assay and its variables do not depend on the physical form of the sample.

2.2.2 Colorimetric Assay of the Silver Nitrate Spray

Initially, a solution of silver nitrate with distilled water at 0.1 M and environment temperature were prepared as the Ref. [11] specified. Fig. 1 shows the recipe for the quantitative to make the solution.

After the preparation of the solution, the samples were broken throughout its height (longitudinal) with the aid of a hydraulic press (Figs. 2 and 3). The objective was to obtain a plant surface of the fracture.

The samples were broken in the respective days (7, 28 and 56 days). The solution of 0.1 M silver nitrate was sprayed on the cracked faces (Fig. 4). A maximum of 15 min was awaited at environment light for the photosynthesis reaction to occur, showing contaminated regions by free chlorides with silver coloration (Fig. 5).

3. Results

In order to make a list and to verify the efficiency of the silver nitrate spray test, a total of 18 samples were molded with 0% chloride content in its mixing water, six for each day of rupture. These samples were the references used as a basis for comparison with other results deriving from the other proportions of chlorides. Table 4 confirms that the reference samples did not have any kind of contamination by free chloride ions in its composition.

It is of general consent in the Brazilian and international literature that the limit of chloride content mixed in a cement paste content cannot exceed

Table 3 Summary of the quantity of molded samples.

Series*	Water/cement ratio	Ratio	Quantity of samples/day of rupture	Day of rupture**	Consumption of cement (g)/six samples	Consumption of salt (NaCl) (g)/six samples	Total of samples/series
0.0%	0.6	1/2.44	6	7, 28 and 56 days	701	0.000	18
0.4%	0.6	1/2.44	6	7, 28 and 56 days	701	2.804	18
0.6%	0.6	1/2.44	6	7, 28 and 56 days	701	4.206	18
0.8%	0.6	1/2.44	6	7, 28 and 56 days	701	5.608	18
1.0%	0.6	1/2.44	6	7, 28 and 56 days	701	7.010	18
2.0%	0.6	1/2.44	6	7, 28 and 56 days	701	14.020	18

*The series are percentages of kitchen salt (NaCl) in relation to the cement mass and mixed in the molding of test samples;
**The days of rupture are counted from the date which the samples were molded.

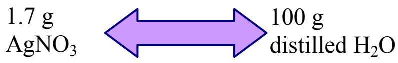

Fig. 1 Recipe of 0.1 M of silver nitrate solution.

Fig. 2 Rupture of the sample.

Fig. 3 Detail of the rupture.

Fig. 4 Silver nitrate spray.

Fig. 5 Part of the whitish surface indicating contamination by free chlorides.

Table 4 Results of percentage of contaminated areas in the 0% samples.

Samples (series 0%)	Contaminated area (%) with samples at 7 days	Contaminated area (%) with samples at 28 days	Contaminated area (%) with samples at 56 days
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	0	0	0
6	0	0	0

Table 5 Results of percentage of the area of contamination in samples with 0.4%.

Samples (series 0.4%)	Contaminated area (%) with samples at 7 days	Contaminated area (%) with samples at 28 days	Contaminated area (%) with samples at 56 days
1	15.86	14.65	12.68
2	15.61	14.73	12.75
3	15.74	14.84	12.66
4	15.88	14.32	12.50
5	15.85	14.97	12.71
6	15.91	14.54	12.65

the value of 0.4% of the weight in cement mass. This information is not totally correct since the types of cement are characterized by different ratios of cement clinker, and will also consequently vary the amount of C_3A (main combining substance with free chloride ions, making them compound chlorides).

Table 5 shows the results that were obtained in the laboratory with cement paste containing 0.4% of chlorides in its composition.

Analyzing the results, it was observed that the samples had an average contamination percentage of 14.38%. This result was unexpected as it was thought that the chlorides would combine with the C_3A of the cement. With these data, the following hypotheses were raised:

- Mixing water could be contaminated by chlorides;
- The aggregate could be contaminated by chlorides.

The author explained the largest number of free chlorides in older samples, the influence of carbonation and commented that the application of the solution of silver nitrate associated with nitric acid completely eliminates the interference of carbonation in interpreting the results because only acknowledge the presence free chlorides. These data lead us to believe that the carbonation may have been one of the main reasons of the increased free chlorides in the samples from 0.4% of chlorides in this research.

Other hypotheses raised to justify the results are the influence of *w/c* ratio, compaction and curing, since these samples were part of the group of specimens that were cured in a moist chamber.

One of the limiting factors for the carbonation is low *w/c* ratio because of the reduction in the porosity of the concrete surface . Noting that the *w/c* ratio used was 0.6, a factor considered high, it leads us to believe that the porosity probably created by the high *w/c* ratio, the possible bad compaction and the curing conditions may have contributed to the carbonation penetration, reinforcing the idea of the interference of CO_2 in the results.

The average contaminated area on the samples with proportions of 0.6% and 0.8 are 17.81% and 44.80% (Tables 6 and 7), respectively.

The cylindrical bodies with 1% and 2% of chlorides had averages over 50% of the area of contamination by chlorides, with respective areas of 57.22% and 95.95% of chlorides on its surface (Tables 6 and 7).

It is interesting that series with 0.8% and two chlorides had significantly higher values of free chlorides comparing with the series with 0.6% and one probably because these series were subjected to submerged cure. It was observed that this increase was due to the higher hydration provided by the type of cure, thus allowing for a possible decrease of the compounds responsible for the chemical combination with chlorides, featuring an unexpected situation, because

Table 6 Results of percentage of contaminated area in samples of 0.6%.

Samples (series 0.4%)	Contaminated area (%) with samples at 7 days	Contaminated area (%) with samples at 28 days	Contaminated area (%) with samples at 56 days
1	20.37	17.34	15.60
2	20.77	17.85	14.97
3	19.56	18.01	15.76
4	19.71	17.90	15.43
5	21.03	17.32	15.55
6	20.55	17.37	15.52

Table 7 Results of percentage of contaminated area in samples of 0.8%.

Samples (series 0.4%)	Contaminated area (%) with samples at 7 days	Contaminated area (%) with samples at 28 days	Contaminated area (%) with samples at 56 days
1	47.89	43.30	42.99
2	47.34	44.90	43.13
3	45.66	44.67	42.55
4	48.05	43.98	42.43
5	47.23	44.35	42.87
6	47.65	44.31	43.13

Table 8 Results of percentage of contaminated area in samples of 1%.

Samples (series 1 %)	Contaminated area (%) with samples at 7 days	Contaminated area (%) with samples at 28 days	Contaminated area (%) with samples at 56 days
1	59.56	56.12	54.39
2	62.43	56.87	54.23
3	61.13	57.43	53.99
4	60.54	56.21	54.81
5	60.77	55.88	55.15
6	59.90	55.98	54.57

Table 9 Results of percentage of contaminated area on samples of 2%.

Samples (series 2 %)	Contaminated area (%) with samples at 7 days	Contaminated area (%) with samples at 28 days	Contaminated area (%) with samples at 56 days
1	98.89	98.70	93.48
2	98.14	95.10	94.01
3	99.44	94.45	94.32
4	96.65	96.10	94.43
5	98.67	93.56	95.08
6	97.90	94.54	93.69

it was believed that the compounds of the cement tend to chemically fix the chlorides present in the concrete.

Results of percentage of contaminated area in samples of 1% and 2% of chlorides are shown in Tables 8 and 9.

4. Conclusions

The analysis of results induces to the following conclusions:

- The method of silver nitrate spraying proved to be applicable in the evaluation of the presence of free chlorides in the samples used in this research. It can be said that the whitish coloration presented by the method indicates the presence of chlorides salts, carbonates or sulphates, among other possible salts aggressive to the structure or to the concrete;
- Among the older samples (56 days), the assessment of the existence of free chlorides should be always linked to the evaluation of the depth of carbonatation that brings along a false result on the presence or not of free chlorides;
- In the case of structures attacked simultaneously by sea water and by CO_2, the analysis with the method of silver nitrate spray becomes complicated because both attacks, CO_2 and chlorides, generate precipitates, which, in the presence of silver nitrate, are quite similar;
- It was reported in every series that the intervals between the ages of 7 days to 56 days, there was a reduction of the contaminated area by free chlorides, possibly due to its combination with C_3A hydrated in the cement.

Acknowledgments

The authors would like to thank UPE/POLI—Universidade de Pernambuco (Polytechnic University of Pernambuco) for its contribution to this research and to the research program (Scientific Initiation).

References

[1] Borelli, E. 2007. “Urbanization and Environmental Quality: The Production Process of the Brazilian Coast Area.” *International Interdisciplinary Journal Interthesis, Florianópoli* 4 (1): 450-8.

[2] IBGE (Brazilian Institute of Geography and Statistics). 2014. “Temperature Levels.” IBGE. Accessed May 6, 2014. http://www.Ibge.gov.br.

[3] Pereira, E., Meneghetti, L. C., Resende, C., and Fabro, G. 2010. “Assessment of the Degree of Reinforcement Corrosion for Different Thicknesses of Coatings.” In *Proceedings of the 52nd Brazilian Concrete Congress,* 250-62.

[4] Neville, A. M., and Brooks, J. J. 2013. *Concrete Technology.* 2a ed.. USA: Trans-Atlantic Publications.

[5] Pontes, R., Monteiro, E. C., Oliveira, R., and Paiva, S. 2011. "Evaluation of Chloride Ions Coastal Zone Recife-PE. Engineering." *Academic Journal of the Faculty of Engineering* 15 (1): 39-49.

[6] Mota, J. M. F., Costa e Silva, A. J., Barbosa, F. R., Andrade, T. W. C. O., and Dourado, K. C. A. 2010. "Assessment of Contamination by Chloride Ions in Concrete Specimens Subjected to Aggressive Conditions." Presented at VI International Congress on Pathology and Rehabilitation of Concrete Structures, Córdoba, Argentina.

[7] Mota, A. C. M. 2011. "Assessment of the Presence of Free Chloride in Mortar Through Colorimetric Method Spray Solution of Silver Nitrate." M.Sc. dissertation, University of Pernambuco.

[8] ABNT (Brazilian Association of Techinical Norms). 1991. *ABNT NBR 11578 Portland composite cement—Specification.* Brazil: ABNT.

[9] ABNT. 1990. *ABNT NBR 11560 Water for Kneading the Concrete to Class I Structures in Central Nucleoelectric—Quality and Control—Specification.* Brazil: ABNT.

[10] ABNT. 1996. *ABNT NBR 7215 Portland Cement—Determination of Compressive Strength.* Brazil: ABNT.

[11] UNI (Italian Organization for Standardization). 1978. *Determination of Chloride Ion Penetration.* Rome: UNI.